

DIIMINE COMPLEXES FOR OLEFIN POLYMERIZATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to transition metal diimine complexes, and in particular, to transition metal diimine complexes useful for olefin coupling and polymerization.

2. Background Art

The chemical industry uses a wide variety of transition metal complexes as catalysts for organic reactions. Olefin polymerization is an important example of such a reaction. While conventional Ziegler-Natta catalysts continue to dominate the industry, highly active metallocene or single-site catalysts that give new polymers with narrow molecular weight distributions, low densities, and good comonomer incorporation are emerging.

Transition metal complexes used to polymerize olefins are normally non-zero-valent metals (e.g., Ti^{4+} , Zr^{4+} , Sc^{3+}) surrounded by anionic ligands (e.g., chloride, alkyl, cyclopentadienyl) that satisfy the valency of the metal. Anionic ligands can dramatically affect catalyst activity and polymer properties. Thus, a catalyst structure can be fine-tuned to give polymers with desirable properties. Furthermore, the anionic ligand will affect the stability of the transition metal complexes.

Metallocene polymerization catalysts contain one or two cyclopentadienyl groups as anionic ligands. These serve to stabilize the active catalytic species, modulate the electronic and steric environment around the active metal center, and maintain the single-sited nature of the catalyst. Polymers with narrow molecular weight and composition distributions are formed from these metallocene catalysts. Such complexes frequently contain substituted

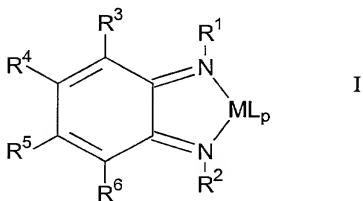
cyclopentadienyl groups. Substituents on the cyclopentadienyl ring may change the geometry and electronic character of the active site.

Another class of anionic ligands includes cyclic, heteroatom-containing ligands which are isolobal to the cyclopentadienyl ring; that is, the orbital interaction of the metal with the ligand is similar in both cases. Examples of such ligands are boraaryl (see, e.g., U.S. Pat. No. 5,554,775), pyrrolyl and indolyl anions (U.S. Pat. No. 5,539,124), azaborolynyl groups (U.S. Pat. No. 5,902,866), phospholyl anions, and tris(pyrazolyl)borate anions.

Ruthenium complexes which include o-quinodiimine ligands have been reported by P. Belser et al, *Inorg. Chem.* 20, p. 3098 (1981). However, the utility of aryl diimine transition metal compounds such as o-quinodiimine and 9,10-phenanthrenequinone diimine transition metal complexes as olefin polymerization catalysts has not been described.

SUMMARY OF THE INVENTION

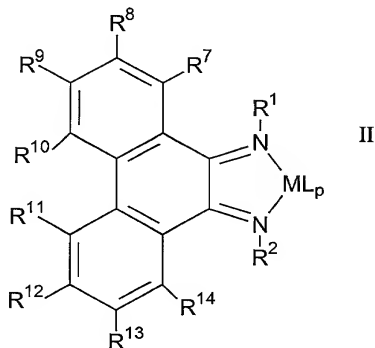
In one embodiment of the present invention, a transition metal catalyst comprising a diimine ligand coordinated to a transition metal is provided. The structure of the diimine ligand coordinated to a transition metal of the present invention is given by:



where M is preferably a metal selected from Groups 3 to 10 of the Periodic Table, more preferably M is a metal selected from Groups 8 to 10 of the Periodic Table, and most preferably M is nickel, palladium, iron, or cobalt; R^1 and R^2 are the same

- or different and are independently selected from hydrogen, a C_{1-10} alkyl group, a C_{6-10} aryl group, or a C_{7-15} aralkyl group each of these groups optionally substituted with a halogen, a cyano group, a C_{1-4} alkoxy group, or a C_{1-4} alkyl group, and with the proviso that not more than 1 of R^1 or R^2 is a hydrocarbon which is branched at the imino-bonded carbon atom; R^3 , R^4 , R^5 , and R^6 are independently hydrogen, a C_{1-10} alkyl group, a C_{6-10} aryl group, a C_{7-15} aralkyl group, C_{1-10} alkoxy, or C_{1-10} dialkylamino group, each of these groups optionally substituted with a halogen, a cyano group, a C_{1-4} alkoxy group, or a C_{1-4} alkyl group, or wherein any two adjacent R^3 through R^6 form a cyclic structure or are part of a larger ring structure, said cyclic structure and said larger ring structure optionally containing one or more heteroatoms, preferably B, N, O, S, or P; L is a neutral or charged ligand; and p is an integer such that complex I is neutral and the valency of M is satisfied. When adjacent R^3 through R^6 substituents form a ring or ring system, the various rings may be saturated, unsaturated, or aromatic. The rings are preferably C_5 or C_6 rings. Preferably, R^1 and R^2 are hydrogen or an unbranched alkyl or aralkyl group.

As examples of a catalyst wherein adjacent R^3 through R^6 constitute a ring system are transition metal catalysts comprising diimine complexes coordinated to a transition metal given by formula II:



where M, R^1 , R^2 , L, and p are defined above; and R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are independently hydrogen, a C_{1-10} alkyl group, a C_{6-10} aryl group, a C_{7-15}

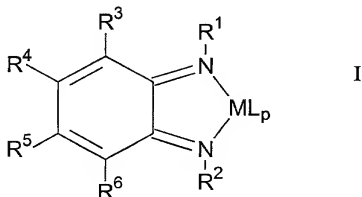
aralkyl group, C₁₋₁₀ alkoxy, or C₁₋₁₀ dialkylamino group, each of these groups optionally substituted with a halogen, a cyano group, a C₁₋₄ alkoxy group, or a C₁₋₄ alkyl group, or wherein any two of R⁷ through R¹⁴, or R¹⁰ and R¹¹ form a cyclic structure or are part of a larger ring structure, said cyclic structure and said larger
5 ring structure optionally containing one or more heteroatoms, preferably B, N, O, S, or P. As is the case with catalysts of the structure of Formula I, additional fused rings may be saturated, unsaturated, or aromatic, and are preferably 5 or 6 membered rings.

In still another embodiment of the present invention, a process for
10 coupling two or more olefins is provided. Such a process includes dimerization, oligomerization, and polymerization. In the processes of the present invention, the complexes described by structures I and II are used to couple olefins.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to presently preferred
15 compositions or embodiments and methods of the invention, which constitute the best modes of practicing the invention presently known to the inventor.

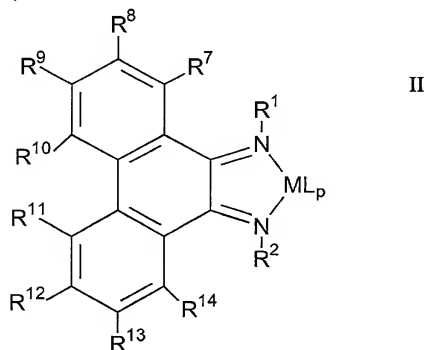
In one embodiment of the present invention, a transition metal catalyst comprising a diimine complex coordinated to a transition metal given by
20 structure I is provided:



where M is preferably a metal selected from Groups 3 to 10 of the Periodic Table, more preferably M is a metal selected from Groups 8 to 10 of the Periodic Table, and most preferably M is nickel, palladium, iron, or cobalt; R¹ and R² are the same

- or different and are independently selected from hydrogen, a C_{1-10} alkyl group, a C_{6-10} aryl group, or a C_{7-15} aralkyl group each of these groups optionally substituted with a halogen, a cyano group, a C_{1-4} alkoxy group, or a C_{1-4} alkyl group, and with the proviso that not more than 1 of R^1 or R^2 is a hydrocarbon which is branched at the imino-bonded carbon atom; R^3 , R^4 , R^5 , and R^6 are independently hydrogen, a C_{1-10} alkyl group, a C_{6-10} aryl group, a C_{7-15} aralkyl group, C_{1-10} alkoxy, or C_{1-10} dialkylamino group, each of these groups optionally substituted with a halogen, a cyano group, a C_{1-4} alkoxy group, or a C_{1-4} alkyl group; or wherein any two adjacent R^3 through R^6 form a cyclic structure or are part of a larger ring structure, said cyclic structure and said larger ring structure optionally containing one or more heteroatoms, preferably B, N, O, S, or P; L is a neutral or charged ligand; and p is an integer such that complex I is neutral and the valency of M is satisfied. When adjacent R^3 through R^6 substituents form a ring or ring system, the various rings may be saturated, unsaturated, or aromatic. The rings are preferably C_5 or C_6 rings. Preferably, R^1 and R^2 are hydrogen or an unbranched alkyl or alkaryl group.

In another embodiment of the present invention, a catalyst comprising a diimine complex coordinated a transition metal given by formula II is provided:



- where M, R^1 , R^2 , L, and p are defined above; and R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are independently hydrogen, a C_{1-10} alkyl group, a C_{6-10} aryl group, a C_{7-15}

aralkyl group, C₁₋₁₀ alkoxy, or C₁₋₁₀ dialkylamino group, each of these groups optionally substituted with a halogen, a cyano group, a C₁₋₄ alkoxy group, or a C₁₋₄ alkyl group, or wherein any two of R⁷ through R¹⁴, or R¹⁰ and R¹¹ form a cyclic structure or are part of a larger ring structure, said cyclic structure and said larger
5 ring structure optionally containing one or more heteroatoms, preferably B, N, O, S, or P. As is the case with catalysts of the structure of Formula I, additional fused rings may be saturated, unsaturated, or aromatic, and are preferably 5 or 6 membered rings.

The one or more anionic or neutral ligands, L, are present in an
10 amount such that the valency of M is satisfied. Examples include unsubstituted and substituted cyclopentadienyl, indenyl, fluorenyl, hydride, halide, alkyl, aryl, aralkyl, dialkylamino, siloxy, alkoxy, pyrrolyl, indolyl, carbazoyl, quinolinyl, pyridinyl, azaborolinyl, boraaryl groups, or the like, and combinations of these. Examples of neutral ligands are carbonyl, η^6 -aryl, η^4 -butadiene, η^4 -cyclobutadiene,
15 η^4 -cyclooctatetraene, tertiary phosphine, and the like. Other examples of suitable anionic or neutral ligands appear in U.S. Pat. Nos. 5,756,611, 5,637,659, 5,637,660, 5,554,775, and 5,539,124, the teachings of which are incorporated herein by reference.

In another embodiment of the invention, the transition metal complex
20 of the present invention further comprises an activator. Generally, the activator converts the complex to a cationically active species. The catalysts are especially valuable for polymerizing olefins, such as ethylene, propylene, and/or other α -olefins such as 1-butene or 1-hexene. Suitable activators are well known in the art. Preferred activators include alumoxanes (i.e., methyl alumoxane, and so-called
25 modified methylalumoxanes, ethyl alumoxane, and diisobutyl alumoxane, alkylaluminum compounds, i.e. triethylaluminum, diethylaluminum chloride, and trimethylaluminum, and the like. Such activators are generally used in an amount within the range of about 0.01 to about 100,000, preferably from about 1 to about 10,000, moles per mole of transition metal complex. Preferred activators also
30 include acid salts that contain non-nucleophilic anions. These compounds generally consist of bulky ligands attached to boron or aluminum. Examples include lithium

tetrakis(pentafluorophenyl) borate, lithium tetrakis(pentafluorophenyl) aluminate, anilinium tetrakis(pentafluorophenyl) borate, and the like. These activators are generally used in an amount within the range of about 0.01 to about 1000, preferably from about 1 to about 10, moles per mole of transition metal complex.

- 5 Suitable activators also include trialkyl or triarylboron compounds such as tris(pentafluorophenyl)boron, tris(pentabromophenyl) boron, and the like. Other suitable activators are described, for example, in U.S. Pat. Nos. 5,756,611, 5,064,802, and 5,599,761, the teachings of which are incorporated herein by reference.

- 10 The catalysts are optionally used with an inorganic solid or organic polymer support. Suitable supports include silica, alumina, silica-aluminas, magnesia, titania, clays, zeolites, or the like. The supports can be pretreated thermally or chemically to improve catalyst productivity or product properties. The catalysts can be deposited on the support in any desired manner. For instance, the
15 catalyst can be dissolved in a solvent, combined with a support, and stripped. Alternatively, an incipient-wetness technique can be used. Moreover, the support can simply be introduced into the reactor separately from the catalyst. The ligand can also be chemically tethered to the support through a suitable linking group.

- In still another embodiment of the present invention, a process for
20 coupling two or more olefins is provided. Such coupling processes include but are not limited to dimerization, oligomerization, and polymerization. In the coupling processes of the present invention, the complexes described by structures I and II are used as catalysts. The process of the present invention comprises:

- 1) mixing in a reaction vessel a solvent, an activator and a catalyst
25 given by formula I or formula II; and
 2) introducing an olefin into the reaction vessel, wherein at least two molecules of the olefin are coupled together.

- The following examples illustrate the various embodiments of the present invention. All reactions are carried out in an inert, air-free atmosphere using
30 vacuum line or dry box. All solvents are dry and deoxygenated. Those skilled in

the art will recognize many variations that are within the spirit of the present invention and scope of the claims.

Example 1

Reaction of (dimethoxyethane)NiBr₂ + 3,4-diaminotoluene in water:

- 5 Approximately, 0.158g (0.0013mmol) of 3,4-diaminotoluene and 10mL deoxygenated water are added to about 0.400g (0.00130mol) of (dimethoxyethane)NiBr₂. The resulting mixture is heated in a 110°C oil bath for two hours. After cooling, 20mL water, 3mL concentrated ammonia, and a threefold excess of sodium hexafluorophosphate (0.655g in 5mL water) are added.
- 10 The mixture turns purple immediately. The purple mixture is stirred for 64 hr at room temperature, during which time a dark purple solid forms slowly. The mixture is filtered to yield a colorless filtrate and the dark solid. The solid is washed with distilled water, then with methanol, and dried under vacuum. A blue solid is obtained (0.44g).
- 15 The blue solid is subjected to the following polymerization testing. A sample of the blue solid is added to a 1-L stainless-steel pressure vessel containing isobutane (500mL) and methylaluminoxane (MMAO)/heptane solution (1.0mL of 6.7% MMAO). MMAO is a modified methylalumoxane available from Akzo-Nobel. Ethylene is fed on demand to maintain a constant pressure in the
- 20 reactor. After 30 min., ethylene uptake is recorded, and the reactor is vented. The results of the polymerization test at various initial temperature is provided in table I. The testing indicates ethylene uptake but no production of solid polymer product. At 40°C, 23g of ethylene was consumed, which calculates to an activity of 784 kg/(g Ni*hr).

5

TEMPERATURE (°C)	ETHYLENE CONCENTRATION (mol %)	CATALYST ACTIVITY (g/(g Ni*hr))
40	25	784
60	25	136
80	25	68

Table I.

10

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.